SIZE-RELATED VARIATIONS IN COAL FLY ASH COMPOSITION AS DETERMINED USING AUTOMATED SCANNING ELECTRON MICROSCOPY

K.A. Katrinak and C.J. Zygarlicke
Energy & Environmental Research Center, University of North Dakota
Grand Forks, North Dakota 58202-9018

Keywords: individual-particle analysis, scanning electron microscopy, coal fly ash

ABSTRACT

A new preparation method for fly ash samples has enabled characterization of particles as small as 0.1 μm in diameter, an order of magnitude less than the lower size limit of 1 μm previously used for automated scanning electron microscopy. The method involves freeze-drying an ash dispersion on vitreous carbon, which provides a very low-contrast background. The smallest particles can thus be imaged and then analyzed using energy-dispersive x-ray spectrometry. Individual particles in this extended size range have been characterized using ash produced through bench-scale combustion of Eagle Butte and Eagle Butte/Kentucky No. 9 blend coals. Distinct size-related compositional variations are evident. Supermicron particles consist largely of calcium- and aluminosilicate-rich minerals. The submicron fraction is dominated by sulfate-, phosphate-, and chloride-rich particles, probably formed through condensation. Their unique composition indicates the importance of including these smallest particles in ash characterization.

INTRODUCTION

Scanning electron microscope analysis of coal and ash samples yields size and composition data on a particle-by-particle basis, information critical in predicting inorganic transformations during combustion. Through automated techniques, hundreds to thousands of individual particles can be chemically analyzed using energy-dispersive x-ray spectrometry and image processing. A minimum of operator effort is thus required to achieve a statistically significant characterization of the sample.

Electron microscope techniques are commonly applied to coal mineral and ash particles with minimum diameters of 1 μm. However, individual-particle analysis is also important for submicron ash particles, which form during combustion from both organically associated elements and from minerals in coal.

Organically associated elements in low-rank coals, including Na, Mg, and Ca, and, to a lesser extent, K, Fe, and Al, commonly vaporize during combustion. Na, Mg, and K are particularly volatile and can condense homogeneously as submicron particles if the ratio of vapor-phase alkali elements to ash surface area is large. These particles usually react with SO_2 to form submicron sulfate particles by the time they reach the outlet of the boiler.

Mineral particles in coal undergo much less vaporization and condensation during combustion. The extent of vaporization depends on the composition of the local gas. If air is not vigorously mixed with the burning coal particles, reducing zones can exist in the flame. Within the reducing zones, SiO_2 can be reduced to SiO, which is volatile. In cooler zones of the furnace, the SiO vapor will oxidize and condense as small SiO_2 particles in much the same way as the vaporized Na species.

Submicron particles can also be produced through size reduction of larger mineral particles when decomposition or fragmentation occurs during heating. When rapidly heated, pyrite fractures and, upon partial oxidation, forms FeS fragments before melting at 1075°C (1). Calcite ($CaCO_3$), siderite ($FeCO_3$), and ankerite ($CaFe[CO_3]_2$) also fragment upon decomposition to form submicron particles (1).

Once formed, submicron particles are difficult to remove from the flue gas stream. When emitted, these fine particles contribute far more to plume opacity per unit mass than do larger particles (2). The effect of the fine particles on plume opacity is maximized because their size distribution peaks near a diameter equal to the wavelength of visible light, the particle size with the greatest amount of scattering per unit mass (3, 4). Understanding of the composition and formation of submicron particles is thus important in mitigating particulate emissions.

Submicron particles are difficult to analyze with automated techniques because their small size places them near the imaging and analytical detection limits of the conventional scanning electron microscope. Using a new sample preparation method involving freeze-drying, individual ash particles with diameters as small as 0.1 μm can be analyzed automatically in the Tracor-Northern automated digital electron microscope (ADEM). The new technique is termed scanning electron microscopy with image analysis (SEM-IA) and is generally similar to computer-controlled scanning electron microscopy (CCSEM). The technique and test results are described below.

METHODS

Sample Preparation. Coal fly ash was produced in a bench-scale drop-tube furnace, as described elsewhere (5). Samples were prepared by freeze-drying a small amount of dispersed particles onto a substrate of vitreous carbon (6). Vitreous carbon is used because its exceptionally smooth surface allows unambiguous identification of small particles. Freeze-drying maintains a uniform separation between particles.

Data Acquisition. The Tracor-Northern ADEM is used for SEM-IA of the freeze-dried sample preparations. It has a spatial resolution of 0.1 μm, allowing analysis of the smallest ash particles. A low accelerating voltage (7 kV) is used to keep the excitation volume within the particles and to improve imaging. Secondary electron imaging (at 10,000x magnification) and derived binary images are used to locate and measure the size of each particle. The image analysis consists of acquiring 25 digital images of each field of view, then averaging them to remove noise.

After an average image has been formed, individual ash particles are automatically sized, then analyzed for chemical composition using energy-dispersive x-ray spectrometry (EDS). The system is configured to detect Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, and Ti. Spectra are acquired for 15 seconds at 300 pA. A relatively low beam current is used to minimize sample damage. Spectra collected using these parameters generally contain sufficient x-ray counts to identify the elemental composition of most submicron particles. The use of a low accelerating voltage results in decreased detection efficiency for many metals, but this does not detract from the analysis of typical submicron particles.

Region-of-interest (ROI) integrated counts and particle-sizing information is saved in the ADEM computer as each field of view, containing approximately 20 individual ash particles, is completed. The light loading of particles is necessary to prevent electron beam overlap onto adjacent particles during analysis. Currently, only approximately 200 particles per sample are analyzed because of the operator time required to manually select each field of view.

Data Reduction. After each sample analysis is complete, the data files are transferred to the Tracor-Northern TN-8500 computer and reduced using the same routines applied to CCSEM data (7). The particle classification program PARTCHAR, developed at the University of North Dakota Energy and Environmental Research Center, was modified to apply more specifically to submicron particles through the inclusion of more sulfate-, phosphate-, and chloride-bearing types and fewer metal-rich types.

RESULTS AND DISCUSSION

Fly ash samples produced from Eagle Butte coal and from a blend of Eagle Butte (70%) and Kentucky No. 9 (30%) coals were analyzed to test the SEM-IA method. The tests were designed to investigate any sampling bias and to compare SEM-IA with CCSEM results for identical samples.

Morphology. Visual inspection of the freeze-dried sample preparations in the ADEM shows that many submicron particles are present. In some instances, several submicron particles are fused together, forming irregularly shaped aggregates. Such aggregates are common in fly ash and probably form at elevated temperatures prior to emission (8, 9). Alternatively, vapor-phase condensation may have occurred following aggregation, smoothing the spherule surfaces together through deposition of coatings. No attempt was made to break up these aggregates, as this would alter the size distribution of the original sample.

Test of Sampling Bias: Eagle Butte Ash. It is possible that operator selection of fields of view could result in overrepresentation of the smallest particles. However, large agglomerated groupings of particles are sometimes present in the sample preparation (probably the result of overloading the sample suspension), and so some operator discretion is necessary. A single freeze-dried preparation of Eagle Butte fly ash was analyzed twice using the SEM-IA method: first using fields of view selected because they contained relatively high proportions of submicron particles, then using randomly selected areas.

Size distributions for the two runs are shown in Figure 1. The results were similar, with both size distributions peaking at a particle diameter of 0.4 μm. The run emphasizing submicron particles has a second peak at a particle diameter of 25 μm, indicating large particle agglomerates were encountered in the areas analyzed. As mentioned above, these agglomerates are an artifact of the sample preparation procedure. The agglomerates are readily identified by their size distribution curve, which is distinctly separate from the curve representing the submicron particles and can easily be removed from the data set after the analysis is completed.

The results of these two runs suggest that the true size distribution of the sample is accurately measured by the SEM-IA method. The peak at diameter 0.4 μm may indicate a uniformity of ash formation processes leading to a consistent particle size.

Comparison of SEM-IA and CCSEM Methods: Eagle Butte Ash. In order to directly compare SEM-IA and CCSEM results, the same freeze-dried dispersion of Eagle Butte fly ash was analyzed using both SEM-IA and CCSEM. In addition, a standard dispersion of the same ash sample was prepared and analyzed using CCSEM. Results are shown in Table 1. Particle compositions for the SEM-IA and CCSEM analyses are completely different, whereas the results for the two CCSEM runs are similar. Particles detected using SEM-IA are predominantly sulfate-, phosphate, and chloride-rich, whereas those detected through CCSEM represent an assortment of minerals, mostly Ca-rich, including Ca aluminate, Ca silicate, gypsum/Al-silicate, Ca-Al-silicate, and others. A minor number of sulfate-rich particles were also detected through CCSEM.

The compositional variations between the SEM-IA and CCSEM data sets reflect the different size ranges represented by the two types of analyses. In the SEM-IA run, the maximum particle diameter in Table 1 was 1.6 μm. Large agglomerates, with diameters of 25 μm and greater, are sample preparation artifacts and were not included in the table. The CCSEM analyses include only particles with diameters >1 μm, and so most of the particles detected using SEM-IA would not be included in the CCSEM results.

It is less clear why the SEM-IA results do not include many particles with diameters in the low end of the CCSEM size range, i.e., those with diameters of 2 to 10 μm. Apparently the fields of view selected for SEM-IA analysis contained few or no particles in this range, in contrast to the areas used for CCSEM. Only a very small area of the sample was used to obtain data for 226 particles

through SEM-IA. The CCSEM analysis of the same freeze-dried preparation included a much larger area (at lower magnification), yielding data for 453 particles. The CCSEM analysis of the standard dispersion included 1013 particles. In the future, SEM-IA runs will be lengthened to make them more directly comparable with CCSEM analyses.

The distinct compositional variation between the submicron size fraction (as measured using SEM-IA) and the supermicron fraction (measured using CCSEM) confirms that they are formed through different processes. Condensation of alkali vapors is evidently the primary mechanism for formation of submicron particles, while the mineral-rich content of the supermicron particles indicates they probably formed through decomposition and fragmentation.

Comparison of SEM-IA and CCSEM Methods: Eagle Butte/Kentucky No. 9 Blend Ash. The SEM-IA method was also evaluated by comparison with CCSEM results for ash from the Eagle Butte/Kentucky No. 9 70%/30% blend. In this case, a freeze-dried dispersion was analyzed using SEM-IA, and a standard dispersion prepared from the same sample was analyzed using CCSEM (Table 2). As for the Eagle Butte ash samples discussed above, the results for the blend ash show distinct size-related compositional variations. The SEM-IA results, which include data for particles with a maximum diameter of 1.6 μm only, are dominated by sulfates, phosphates, and chlorides. No typical coal minerals were identified in the SEM-IA data set. Almost half of the particles identified using SEM-IA did not fit into any of the defined compositional categories and were thus classified as "unknown." These unclassified particles contain Si, Al, Mg, Ca, Na, S, Cl, and other elements in varied proportions and may represent coated mineral particles.

The CCSEM data for the blend ash indicate a range of minerals. As for the Eagle Butte ash, the mass of the blend ash analyzed using CCSEM is concentrated in particles with diameters from 1 to 10 μm. The CCSEM results for the blend ash indicate more sulfate-rich particles and fewer Ca-bearing particles than do the results for the Eagle Butte ash.

CONCLUSIONS

SEM-IA results clearly indicate a size-related shift in composition, from mineral-rich particles in the supermicron fractions, to sulfate-, phosphate-, and chloride-rich particles in the submicron fractions of both Eagle Butte and Eagle Butte/Kentucky No. 9 blend ashes. The distinct compositions of the two size fractions confirm that they form through different processes, probably primarily fragmentation and coalescence for the supermicron particles and vaporization and condensation for the submicron particles. The unique compositions of particles in the submicron fraction suggest that individual-particle analysis of these smallest particles is essential to achieving an overall understanding of the transformations occurring during combustion.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under Cooperative Agreement No. DE-FC21-86MC10637.

REFERENCES

1. Raask, E. "Mineral Impurities in Coal Combustion," Hemisphere Publishing Corp.: New York, 1984.

2. Balfour, D.A.; Meserole, F.M.; Defries, T. "Utility Stack Opacity Troubleshooting Guidelines," final report; EPRI Research Project No. 2250-3, 1991.

3. Mie, G. "Beitrage zur Optik truber Medien speziell kolloidaler Metallosungen," *Ann. Phys.* **1908**, *25*, 377-445.

4. Bohren, C.F.; Huffman, D.R. "Absorption and Scattering of Light by Small Particles," John Wiley & Sons: New York, 1983, 530 p.

5. Zygarlicke, C.J.; McCollor, D.P. "The Effect of Coal Blending on Inorganic Transformations: A Study of an Eagle Butte/Kentucky #9 Blend," *In* Proceedings of the Ninth Annual International Pittsburgh Coal Conference; 1992, pp 775-789.

6. Katrinak, K.A.; Brekke, D.W.; Hurley, J.P. "Freeze-Dried Dispersions for Automated Scanning Electron Microscope Analysis of Individual Submicron Airborne Particulates," *In* Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America; San Francisco: San Francisco Press, Inc., 1992, pp 408-409.

7. Zygarlicke, C.J.; Steadman, E.N. "Advanced SEM Techniques to Characterize Coal Minerals," *Scanning Microscopy Intl.* **1990**, *4* (3), 579-589.

8. Hazrati, A.; Schrodt, J.T. "Microcharacterization of Micron/Submicron Fly Ash from a Pulverized-Dry-Coal-Burning Power Plant," *Surf. Interface Anal.* **1988**, *13*, 142-148.

9. Kaufherr, N.; Lichtman, D. "Comparison of Micron and Submicron Fly Ash Particles Using Scanning Electron Microscopy and X-Ray Elemental Analysis," *Environ. Sci. Technol.* **1984**, *18* (7), 544-547.

Table 1. Compositions, in Weight Percentages, for Eagle Butte Fly Ash

Particle Type	SEM-IA Run (freeze-dried)	CCSEM Run (freeze-dried)	CCSEM Run (standard)
Quartz	0	3.8	6.5
Iron Oxide	0	1.6	0.2
Periclase	1.6	0	0
Alumina	0	0.3	0
Calcite	0	0.7	0.8
Dolomite	0	3.0	5.0
Kaolinite	0	1.5	0
Ca Al-Silicate	0	5.0	6.2
Na Al-Silicate	0	4.3	2.3
Mixed Al-Silicate	0	1.6	1.1
Ca Silicate	0	6.5	2.6
Ca Aluminate	0	17.3	24.4
Sulfate-Rich	42.7	2.0	1.3
Phosphate-Rich	16.2	0	0
Chloride-Rich	11.4	0	0
Gypsum/Al-Silicate	0	5.8	2.8
Si-Rich	0	0.6	1.6
Ca-Rich	0	5.9	2.9
Ca-Si-Rich	0	2.2	2.6
Unknown	28.1	37.7	39.9
TOTALS	100.0	100.0	100.0

Table 2. Compositions, in Weight Percentages, for Eagle Butte/Kentucky No. 9 Blend Ash

Particle Type	SEM-IA (freeze-dried)	CCSEM (standard)
Quartz	0	6.5
Iron Oxide	0	0.5
Rutile	0	0.1
Alumina	0	0.1
Calcite	0	1.4
Ankerite	0	0.2
Kaolinite	0	6.3
Montmorillonite	0	1.8
K Al-Silicate	0	0.5
Fe Al-Silicate	0	3.9
Ca Al-Silicate	0	9.2
Na Al-Silicate	0	9.7
Aluminosilicate	0	0.1
Mixed Al-Silicate	0	2.4
Ca Silicate	0	1.9
Ca Aluminate	0	1.4
Sulfate-Rich	24.5	17.7
Phosphate-Rich	13.4	0
Chloride-Rich	14.7	0
Gypsum/Al-Silicate	0	3.0
Si-Rich	0	3.0
Ca-Rich	0	0.1
Ca-Si-Rich	0	0.6
Unknown	47.4	29.4
TOTALS	100.0	100.0

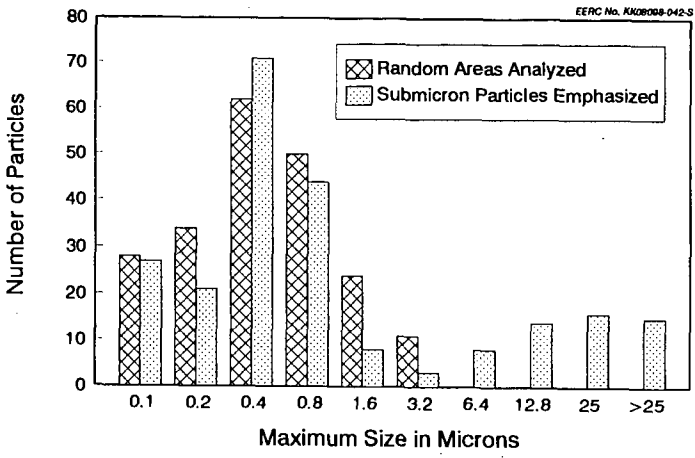

Figure 1. Size distributions for SEM-IA results for Eagle Butte ash, using a freeze-dried sample preparation.